A Method Using Simultaneous Equations for Estimating Percent Concentration of Kraft Effluent in Marine Receiving Waters

G. L. Greer

Department of Fisheries and Oceans
Fisheries Research Branch
West Vancouver Laboratory
4160 Marine Drive
West Vancouver, British Columbia, Canada V7V 1N6

December 1983

Canadian Technical Report of Fisheries and Aquatic Sciences No. 1224

Canadian Technical Report of Fisheries and Aquatic Sciences

Technical reports contain scientific and technical information that contributes to existing knowledge but which is not normally appropriate for primary literature. Technical reports are directed primarily toward a worldwide audience and have an international distribution. No restriction is placed on subject matter and the series reflects the broad interests and policies of the Department of Fisheries and Oceans, namely, fisheries and aquatic sciences.

Technical reports may be cited as full publications. The correct citation appears above the abstract of each report. Each report is abstracted in *Aquatic Sciences and Fisheries Abstracts* and indexed in the Department's annual index to scientific and technical publications.

Numbers 1–456 in this series were issued as Technical Reports of the Fisheries Research Board of Canada. Numbers 457–714 were issued as Department of the Environment, Fisheries and Marine Service, Research and Development Directorate Technical Reports. Numbers 715–924 were issued as Department of Fisheries and the Environment, Fisheries and Marine Service Technical Reports. The current series name was changed with report number 925.

Technical reports are produced regionally but are numbered nationally. Requests for individual reports will be filled by the issuing establishment listed on the front cover and title page. Out-of-stock reports will be supplied for a fee by commercial agents.

Rapport technique canadien des sciences halieutiques et aquatiques

Les rapports techniques contiennent des renseignements scientifiques et techniques qui constituent une contribution aux connaissances actuelles, mais qui ne sont pas normalement appropriés pour la publication dans un journal scientifique. Les rapports techniques sont destinés essentiellement à un public international et ils sont distribués à cet échelon. Il n'y a aucune restriction quant au sujet; de fait, la série reflète la vaste gamme des intérêts et des politiques du ministère des Pêches et des Océans, c'est-à-dire les sciences halieutiques et aquatiques.

Les rapports techniques peuvent être cités comme des publications complètes. Le titre exact paraît au-dessus du résumé de chaque rapport. Les rapports techniques sont résumés dans la revue *Résumés des sciences aquatiques et halieutiques*, et ils sont classés dans l'index annual des publications scientifiques et techniques du Ministère.

Les numéros 1 à 456 de cette série ont été publiés à titre de rapports techniques de l'Office des recherches sur les pêcheries du Canada. Les numéros 457 à 714 sont parus à titre de rapports techniques de la Direction générale de la recherche et du développement, Service des pêches et de la mer, ministère de l'Environnement. Les numéros 715 à 924 ont été publiés à titre de rapports techniques du Service des pêches et de la mer, ministère des Pêches et de l'Environnement. Le nom actuel de la série a été établi lors de la parution du numéro 925.

Les rapports techniques sont produits à l'échelon régional, mais numérotés à l'échelon national. Les demandes de rapports seront satisfaites par l'établissement auteur dont le nom figure sur la couverture et la page du titre. Les rapports épuisés seront fournis contre rétribution par des agents commerciaux.

Canadian Technical Report of Fisheries

and Aquatic Sciences No. 1224

December 1983

A METHOD USING SIMULTANEOUS EQUATIONS FOR ESTIMATING PERCENT CONCENTRATION OF KRAFT EFFLUENT IN MARINE RECEIVING WATERS

G. L. Greer

Department of Fisheries and Oceans

Fisheries Research Branch

West Vancouver Laboratory

4160 Marine Drive

West Vancouver, British Columbia

Canada, V7V 1N6

(c)Minister of Supply and Services Canada 1983

Cat. No. Fs 97-6/1224 ISSN 0706-6457

ABSTRACT

Green, G. L. 1983. A method using simultaneous equations for estimating percent concentration of kraft effluent in marine receiving waters. Can. Tech. Rep. Fish. Aquat. Sci. 1224: iv + 23 p.

Details of a method are presented for estimating the receiving water concentrations of kraft mill effluent discharged into costal marine waters. The method is based on the proportionate mixing of three water sources in the surface zone of a coastal inlet and the assumption of a simple, two-layer flow model of estuarine circulation. The three source waters were: effluent discharged by the mill, fresh water from nearby rivers or streams, and higher salinity water from the inward flowing subsurface zone. The properties used to identify the source waters were color and salinity. The percent concentration of the three source waters in mixture are derived by simultaneous equations. Application of the method to a small area in a British Columbia coastal inlet receiving effluent from a kraft mill indicated a highly stratified distribution of effluent with concentrations varying up to 40% at the surface and diminishing to less than 1% at 2.5 m depth. A substantial addition of freshwater to the surface and upper portions of the water column with attendant greater dilution of effluent was observed during several days of rainfall and high stream run-off.

Key words: kraft mill effluent, water mixing, effluent dispersion, salinity, color.

RÉSUMÉ

Greer, G. L. 1983. A method using simultaneous equations for estimating percent concentration of kraft effluent in marine receiving waters. Can. Tech. Rep. Fish. Aquat. Sci. 1224: iv + 23 p.

Présentation détaillée d'une méthode servant à calculer les concentrations, dans les eaux réceptrices, de l'effluent d'une usine de fabrication de pâte kraft déversé dans un secteur côtier. La méthode repose sur le mélange en proportions identiques de trois sources d'eau dans la zone de surface d'un goulet côtier et sur l'hypothèse d'un modèle simple d'écoulement à deux couches pour la circulation estuarienne. Les trois sources d'eau étaient: l'effluent déversé par l'usine, l'eau douce des rivières ou des ruisseaux avoisinants et l'eau très salée de la couche sous la surface s'écoulant vers l'intérieur. La couleur et la salinité ont servi à identifier les eaux des différentes sources. Le pourcentage de concentration des eaux des trois sources à l'intérieur du mélange est établi à partir d'équations simultanées. L'application de la méthode à un secteur limité d'un goulet côtier de la Colombie-Britannique où se déverse l'effluent d'une usine de fabrication de pâte kraft a mis en lumière une répartition de l'effluent très stratifiée et montré que la concentration atteignait jusqu'à 40 % à la surface et diminuait jusqu'à moins de 1 % à 2,5 m de profondeur. Pendant plusieurs jours de pluie et de ruissellement importants, on a observé l'addition d'une grande quantité d'eau douce aux couches superficielles et supérieures de la colonne d'eau et, partant, une dilution plus grande de l'effluent.

Mots-clés: effluent d'une usine de pâte kraft, mélange de l'eau, dispersion de l'effluent, salinité, couleur.

INTRODUCTION

The usual practice of effluent disposal by pulp mills located on British Columbia coastal inlets is by discharge into adjacent marine waters. Two methods of discharge prevail: one is at depth via submarine diffuser, and the other by sewer(s) located at elevations within or near the range of tidal excursions, i.e. surface outfall. Development of suitable methods for estimating the concentation of pulpmill effluent in marine receiving waters to assist determining the impact of this waste on resident fish and other species has been a continuing problem. The subject of the present report is a proposed method for field application which takes into account basic features of coastal inlet circulation in British Columbia.

Coastal inlets on the B.C. mainland and the western margin of Vancouver Island typically receive large inflows of fresh water from rivers at the head. They are, thusly, characterized by a marked vertical stratification of salinity and also density since density in these waters is determined largely by salinity (Pickard 1961). Because the pulping process uses fresh water, the density of pulpmill effluent can be similar to or less than the density of inlet surface water. Oceanographically, effluent with this physical characteristic will behave much as a freshwater stream and add to the brackish upper layer (Tully 1949). Accordingly, effluent from surface outfalls in particular can be expected to disperse largely in the low salinity regions of the upper water column and undergo a net transport seaward. In the course of seaward transport, dilution and dispersion of the effluent will occur through the processes of eddy diffusion by vertical and lateral mixing, and through advection due to the action of wind and tide.

Species of particular interest that could encounter and experience deleterious effects of pulpmill effluent in their natural environment are the juvenile Pacific salmonids which utilize British Columbia coastal inlets as nursery areas during their outmigration to sea. Most pulpmills now use the kraft process (wood digestion in a caustic mixture of sodium salts) and considerable laboratory research using salmonids has been directed to acute toxicity studies (e.g. Davis and Mason 1973; McLeay 1976; Gordon and McLeay 1977) of kraft mill effluent and to sublethal effects of this effluent on various aspects of physiology and behavior of salmonids (see summary by Davis 1976). In studies such as these, the biological responses typically are expressed in terms of the percent whole effluent to which the fish were exposed. If the results of acute toxicity and sublethal studies in the laboratory are to have predictive value in assessing possible effects of kraft mill effluent on fish and other organisms in their natural habitats, it is desirable to be able to estimate the quantity of whole effluent in receiving waters in the units of concentration used in laboratory studies.

Mainly four techniques have been applied in estimating the quantity of puplmill effluents in receiving waters: the Pearl-Benson or nitroso method (Barnes et al. 1963; Waldichuk 1964), fluorometry (Baumgartner et al. 1971, 1974; Wilander et al. 1974; Josefsson and Nyquist 1976), UV spectrophotometry (Mrkva 1969; Wildish et al. 1976), and colorimetry with the effluent itself

(Werner and Hyslop 1967). These techniques have been successful in determining the relative effluent loading and/or the tracking of effluent in receiving waters, but the units of concentration derived cannot easily be related to the units of percent concentration used in most effluent toxicity and sublethal studies. In order that estimates of receiving water concentration can be derived, it is essential that any effluent measuring technique also be applied to the undiluted effluent before discharge, as was done by Waldichuk (1964) in studies of effluent dispersion in Stuart Channel, B.C. Further, since the effluent property being measured usually can arise from non-mill sources as well (e.g. Barnes et al. 1963; Wilander et al. 1974), estimation of the contribution of that property from these other sources needs to be accounted for.

An alternative method for determining the concentration of pulpmill effluent in marine receiving waters is contained in the study by Ketchum (1967) on sources of enrichment in the New York Bight. In that study, the proportions of water from three sources undergoing mixing were determined using two properties of the source waters and a system of three simultaneous equations. The three source waters identified in mixtures were the brackish water resulting from dilution by the Hudson and Raritan Rivers, the surface coastal water entering from eastward, and the deep ocean water brought in by countercurrent in the estuarine-type circulation. The method used by Ketchum bears directly on the mixing and dilution of pulpmill effluent discharged from surface outfalls into coastal inlets and presents the additional feature that some information can be gained on the mixing and dispersing characteristics of the receiving water body. An adaptation of this method was developed for estimating the concentration of kraft effluent in receiving waters adjacent to the surface outfall of the Port Mellon, B.C., pulpmill and is elaboratored below.

BASIS OF METHOD

The method of study by Ketchum (1967) stems from a technique that has been applied in oceanographic studies for some time (Proudman 1953) whereby the mixing of ocean water masses is represented by the T-S (temperature-salinity) correlation diagram. For the case of mixing of three water masses A, B, and C, each having temperature and salinity T_a, S_a; T_b, S_b; and T_c, S_c; the proportionate composition of each of the source waters in the mixture can be derived from the temperature and salinity values of the source water masses and the water mixture by solving the following simultaneous equations:

$$T_aA + T_bB + T_cC = T$$
$$S_aA + S_bB + S_cC = S$$
$$A + B + C = 1$$

where T and S are the temperature and salinity of the mixture and A, B, and C are the proportions of each water mass in the mixture (Mamayev 1975). Alternatively, a graphic solution can be derived using the T-S correlation diagram.

The two properties identifying the three source waters must be conservative. Temperature is a conservative property of large water masses on the open ocean but, unlike salinity, it is not a conservative property of relatively shallow, inshore waters. In Ketchum's (1967) study on sources of enrichment in the New York Bight the second property chosen, in addition to salinity, was total phosphorus. Although total phosphorus concentration could be altered by processes other than mixing, thereby not fulfilling the requirement of a conservative property, departure from conservativity was judged by him to be relatively minor. A noticeable feature of kraft mill effluent is the intense brown color which arises mainly in the bleaching process through the action of chlorine on lignin in the brown stock. Color can be easily quantified by the visual comparison method (APHA 1971) and requires simple apparatus. Effluent color increases with increasing pH of the dilution water but since the pH of marine waters is relatively constant, the color of effluent diluted in marine receiving waters should reasonably satisfy the requirement of conservation and be suitable as one of the identifying properties (Werner and Hyslop 1967).

The freshwater-marine system on which many British Columbia coastal pulp mills are located is not unlike the system studied by Ketchum (1967). It is the freshwater inflow that gives rise to the estuarine-type circulation in which the net seaward surface outflow and subsurface inflow is accompanied by upward mixing (entrainment) of subsurface zone water into the surface zone (Bowden 1967; Pickard 1961, 1963). Thus, in the vicinity of a pulp mill with effluent discharged via surface outfall, the surface zone can be described as a receiving water body undergoing mixing of water from three sources, namely, freshwater streams, pulpmill effluent, and subsurface zone water. On a scale of relative magnitude of the two properties color and salinity, each water source can be characterized as follows: freshwater source(s) - low color, low salinity; effluent - high color, low salinity; subsurface inlet water - low color, high salinity. In graphical representation, the color and salinity of each water source will locate the apices of a color-salinity correlation triangle. Any given mixture comprised of the source waters will have a unique combination of the two properties that will fall within or on the boundaries of the correlation triangle from which the proportionate composition can be derived graphically. It is more practical, however, to derive the proportion of the source waters in mixture by solution of simultaneous equations of the form given above.

Representative values of color and salinity for the three water sources undergoing mixing become the coefficients on the left side of the first two equations. Determination of representative values for the freshwater sources(s) is straightforward. For the mill effluent, the two properties are determined on an effluent mixture composited according to the flow volume in each process stream sewered by the mill. Determining the color and salinity coefficients of seawater from the subsurface zone presents the greater problem of deciding the depth delimiting the zone of mixing. Most B.C. inlets are deep and the non-tidal, estuarine circulation characteristic of them (Pickard 1961, 1963) probably resembles the two-layer flow with entrainment model described by Bowden (1967). This model typifies the circulation in Alberni Inlet, B.C., for example, where Tully (1949) regarded the base of the halocline as the depth at which the transfer of water from the subsurface zone was by entrainment only with mixing taking place in the halocline. At the same time, it is likely some small proportion

of low salinity water from the seaward-flowing surface zone mixes downward into the subsurface inflow in inlets with this type of circulation (Bowden 1967). Thus, to obtain the coefficients for this water source, it becomes necessary to determine the salinity structure of the effluent-receiving waters and record the color and salinty of the subsurface water at the depth corresponding to the base of the halocline.

It is acknowledged that the estuarine circulation is likely more complex than suggested here and the elementary description of the dynamics involved should be regarded as a first approximation. Especially in the very shallow, near-shore areas of effluent-receiving waters, the effect of wind and tide on stratification and mixing in the water column can be pronounced and may cause substantial departure from the simple, two-layer flow model.

MATERIALS AND METHODS

Study Area

The proportions of the three source waters (freshwater streams, pulpmill effluent, subsurface inlet water) present in mixtures in the surface zone were estimated in effluent-receiving waters comprising a 0.38 km^2 area adjacent to the kraft mill at Port Mellon, B.C. The mill is located between two small river systems which flow into Thornbrough Channel on the west side of Howe Sound (Fig. 1). Fresh water used by the mill is obtained from Rainy River to the north of the mill site. About 1 km south of the mill, McNair and Dakota Creeks form a confluence approximately 100 m inland and enter Thornbrough Channel along a common course. A permanent log storage and sorting area extends along the shore south of the mill.

The direction of prevailing winds in Thornbrough Channel are constrained by the mountainous terrain and can be southerly or northerly. Winds were light (ca. 5 km/hr max) and from the south during all sampling of the water mixtures.

Mill Operation

The Port Mellon mill uses hemlock, fir, and cedar wood chips digested in a solution of caustic soda and caustic sulfide in a ratio of approximately 4:1 (kraft process). In the production of fully bleached pulp, the bleaching sequence consists of five stages: chlorination, first caustic extraction, first chlorine dioxide, second caustic extraction, and second chlorine dioxide. The rated production capacity for fully bleached pulp is 455 air dry tonnes per day. The mill also produces unbleached and semi-bleached pulp employing fewer stages in the bleaching sequence.

Alkaline waste is discharged via a 0.75 m diameter pipe into a ditch on the beach. The bottom of the pipe is at an elevation of about 1.2 m relative to tidal heights at Point Atkinson, B.C., and is submerged at tidal

heights exceeding approximately 2 m. The acid bleach waste pipe leads into a small lagoon and discharges at a depth approximately 4.5 m below low tide level. The combined discharge from the two sewers is of the order 113 x 10^3 m^3/day.

Water mixtures: sample collection and determination of properties

Water mixtures were collected at depths of 0, 0.5, 1.5, and 2.5 m at four stations along each of three transects aligned more or less perpendicularly to the shoreline adjacent to the mill site and extending to about one-third the width of Thornbrough Channel (Fig. 1). Station positions on each transect were approximately equal distance apart. The laying out of the transects and station positions depended on the availability of charted landmarks and closing headlands for taking ranges and compass bearings.

Water sampling was done once each day on the days August 23-26 inc. and August 28-30 inc., 1978, usually between 1300 and 1600 h. Water below the surface was collected with a 2-L Vandorn bottle and samples transferred to 75 mL screw-cap bottles. Samples at 0 m were taken about 10 cm below the surface using the 75 mL bottles.

Color was determined by the visual comparison method with PtCo standard (APHA 1971). Salinity measurements were made with a Guildline Instruments Model 8400 AutoSal salinometer for water with salinity >5‰ or a YSI Model 33 S-C-T meter for lower salinity water.

Source waters: determination of coefficients

Color and salinity determinations were made during the August 23-26 and 28-30 sampling periods on water collected 1-2 times daily from the three freshwater streams adjacent to the mill. The freshwater samples were taken in mid-stream well above the reach of the tide. Samples from the alkaline and acid bleach waste streams were composited in the proportions specified by mill personnel as follows: alkaline 68%, 1st caustic 2%, combined bleach 30%. The combined bleach consisted of bleach plant streams mixed as follows: chlorine 60%, 1st chlorine dioxide 25%, and 2nd chlorine dioxide 15%.

Color and salinity representative of the subsurface zone of the effluent receiving waters were determined from color and salinity data obtained in June 1977 (Greer 1978 and unpub. obs.) and in the present study. Water was collected by conventional hydrographic methods using Nansen reversing bottles at depths, 0, 2, 3, 6, 8, 10 and 20 m at stations on the west side of Thornbrough Channel (Greer 1978). For the three hydrographic stations closest to the transect sampling area (Stns. HS-3, -4, -5; Fig. 1), color and salinity profiles were plotted from the data for both years and the color and salinity recorded for the depth judged to be nearest the bottom of the halocline. Means (±S.E.M) for color and salinity were computed separately for each of the hydrographic sampling periods June 1977 and July-August 1978 (Table 1).

Measurement error

The maximum error in salinity measurements was estimated to be of the order ± 0.5‰ and is based on one half the smallest scale division for reading

salinity with a YSI S-C-T meter. The more accurate AutoSal salinometer was used for most of the salinity determinations and also provided a secondary standard for the YSI salinometer.

The measurement error for color determinations was estimated to be ± 3 PtCo units in using a color standard which ranged from 0-50 PtCo units and with standard increments of 5 PtCo units. With practice, color determinations within approximately one-half the standard increment could be made. This error applies to the samples when diluted which, for composited effluent, was always 100-fold and for the samples of water mixtures ranged 5-20 fold.

Data analysis

Solution of the simultaneous equations was by conventional matrix inversion and multiplication using a Hewlett-Packard model 9825A program. Color and salinity coefficients for the effluent and freshwater sources were derived for each sampling day, but a single pair of values for the subsurface zone coefficients was used for all computations.

RESULTS

Derivation of coefficients for the source waters

Subsurface zone

The subsurface zone salinity structure of the effluent receiving waters adjacent to the mill on the west side of Thornbrough Channel was similar for the June 1977 and July-August 1978 hydrographic sampling periods. For the three stations HS-3 to HS-5 (Fig. 1, Table 1), the mean salinity at the bottom of the halocline ranged from 25.6-26.2‰ and mean color 4.3-7.3 PtCo units. The mean halocline depth was shallower by approximately 1-2 m during the July-August 1978 sampling than in June 1977 (Table 1), which latter month tends to have higher rainfall locally. Since the July-August hydrographic sampling closely preceded the water mixtures sampling, and Stns. HS-3 and HS-5 were well outside the relatively small area bounded by the transects (Fig. 1), the mean color and salinity values determined for Stn. HS-4 (5 PtCo units and 26.2‰, resp.) were judged the more representative estimate of the subsurface zone coefficients and were used in all computations deriving the proportions of source waters in mixtures. This value of salinity (26.2‰) was not greatly different from the mean salinity of 25.9‰ obtained from the June hydrographic sampling the previous year. Moreover, a discrepancy of 0.3‰ salinity in the subsurface zone water would make little difference in the derived concentration of effluent (see Discussion).

Kraft mill effluent

The effluent salinity coefficient for each sampling day was the mean of replicated effluent salinity determinations for that day. The mean

salinity of composited effluent ranged from 0.7-1.0‰ (Table 2).

The mean color of composited effluent averaged over the sampling period was about 1900 PtCo units with large departures from the mean occurring on three days (Fig. 2). While not atypical of mills processing wood furnish in batch, the presence of these large variations in effluent color nevertheless makes selection of a value representative of mill output of color difficult. In an attempt to account to some extent for variations of color discharged by the mill over time, the value of the effluent color coefficient was selected arbitrarily by interpolating from the data in Fig. 2 the color at the time each day's sampling of the receiving water mixtures commenced (Table 2). Possibly a more accurate solution to the equations could be obtained if interpolation of the effluent color coefficient incorporated an estimate of a time lag between variations of color at the point of effluent discharge and similar variations of color in the receiving waters. However, lags could not be distinguished in the highly variable time courses of color plotted from the present data for the receiving water sampling stations.

Freshwater streams

The color and salinity of the freshwater sources (Rainy River, McNair and Dakota Creeks; Fig. 1) are shown in Table II for each of the sampling days. A brown humic stain was always visible in Dakota Creek and accounts for the higher color values recorded for that freshwater source compared to McNair Creek and Rainy River. The higher color values recorded for all three of the streams through August 24-26, inc. (Table 2), occurred during frequent and very heavy rain showers. Salinity of the stream waters was 0‰ except on August 28 when 0.8°‰ was recorded for McNair Creek. Since the tide was not high enough to intrude into the sampling location in McNair Creek, this salinity value is likely in error. The presence of a small error in the freshwater salinity coefficient will, however, have little effect on the derived value of effluent concentration (see Discussion). The color and salinity coefficients used for the freshwater sources were the means of the daily measurements pooled for the three streams and were calculated for each sampling day.

Proportion of the source waters in mixture

Vertical distribution of source waters

An example is presented in Table 3a showing the simultaneous equations set out in matrix form and the derived concentration of the source waters for a water mixture sample at Stn. G-1, 0 m depth, on August 30. The results for depths 0-2.5 m at Stns. G-1 and G-2 (Fig. 1) presented in Table 3b show the main feature in the vertical distribution of the three source waters, namely, that the concentrations of effluent and freshwater in mixture decrease with depth and are inversely related to the concentation of subsurface zone water in mixture.

Pulpmill effluent

Contour lines constructed from effluent concentrations estimated in the receiving water mixtures and plotted for all stations and depths for each

of the six sampling days were used to determine both the vertical and horizontal distribution of effluent along each transect. Typical features of the distribution of effluent in the 0-2.5 m portion of the water column are illustrated for three sampling days in Fig. 3a-c.

The highest concentrations of effluent ranged from 10-40% and were encountered mainly along Transect OD (Fig. 1) which was the transect nearest the outfall. Effluent concentrations between the surface and 2.5 m depth were lowest along Transect C and intermediate along Transect G, suggesting the main path of effluent dispersion was southerly (i.e. seaward) along the axis of Thornbrough Channel. However, the location of highest surface concentrations along Transects OD and G varied on different days indicating a pooling of effluent and a dispersion path that probably follows a changing course in its seaward movement.

The pooling of effluent in the surface layer appeared to be affected by the state of the tide (see insets to Fig. 3). Although high effluent concentrations ranging from about 5 - 40% were present at the surface on both ebb and flood tides, on ebb tides the highest surface concentrations tended to be farther offshore along a given transect with concentrations in the water column diminishing sharply to about 1% by 1 m depth (e.g. compare Figs. 3a, 3b with Fig. 3c). On flood tides, surface effluent concentrations nearer the shore were typically high (up to 40%) but at 1 m depth ranged from 5-10% and became less than 1% towards the center of the channel (e.g. Fig. 3c).

The heavy rainfall that occured over about one-half of the sampling period confounds the apparent effect of tides on dispersion of the effluent because of the potentially greater dilution of the surface zone by freshwater stream run-off into the receiving waters. The substantial addition of freshwater to the upper portion of the surface zone during the three days of August 24-26 is illustrated by the data for Transect OD (%F, Table 4) and is most evident at the depths 0-1.5 m. Within this three-day period, however, when daily sampling was carried out on the tidal sequence flood-ebb-flood, there was a tendency for effluent concentrations (%K, Table 4) to be lower on the ebb tide than on the preceding and following flood tides. The negative values of derived effluent concentrations for some stations and depths occurred on all the sampling transects (see Table 4) but only during the days of rainfall. This anomaly will be treated in Discussion.

Stratification of effluent in the water column ranged from highly stratified (Fig. 3b, Transects OD, G) to nearly vertically homogeneous (Fig. 3a, Transect C). In contrast to the pooling of effluent in the surface layer, stratification over the 0-2.5 m water column did not appear to be associated with the state of the tide. Cells of effluent at concentrations higher or lower than the surrounding water were not uncommon. Where for given depths lower effluent concentrations relative to the surface occurred more or less directly beneath the highest surface concentrations (e.g. Transects OD and G; Figs. 3b, c), the dispersion process would appear to be largely by vertical mixing. The presence of cells of uncontaminated water (Transect G, Fig. 3a) or cells of higher concentrations of effluent (Transect OD; Figs. 3a, c) however, suggests dispersion could also occur by mass transport. These cells also indicate the process of interleaving of waters with different effluent concentrations. This process could result from tidal (and wind-driven) currents transporting less contaminated water into the

study area which may then flow over water with the relatively high effluent concentrations.

DISCUSSION

The present method for estimating kraft mill effluent concentrations in marine receiving waters has associated with it at least two sources of error: (1) measurement error in the quantitative determination of the two identifying properties in the three source waters and in water mixtures, and (2) error in the assumption that the three source waters undergo mixing in the small-scale, near-shore area sampled according to the two-layer flow model of estuarine circulation. An additional source of error, sampling error, would also be present but cannot be estimated because replicate sampling was not employed in the temporal sampling scheme used.

The partitioning of measurement errors to the derived concentration of waters in a mixture cannot be easily generalized quantitatively. Qualitatively, however, measurement error associated with one of the properties of the source waters will be distributed mainly to the derived concentration of that water in the mixture which makes the greatest contribution of that property to the mixture. Thus the derivation of effluent concentrations will be most susceptible to measurement error in the color of the source waters but usually not to error associated with measurement of the salinity. Hence, selection of either of the mean values 26.2‰ or 25.9‰ (Table 1) for the subsurface zone salinity coefficient would have minor effect on the outcome of the computations.

An impression of the effect of measurement error present in the source water color coefficients can be gained from the example presented in matrix form in Table 3a. To demonstrate the worst case, if errors of the expected magnitude described in Methods are applied in the same sign to all the color coefficients (i.e. k, f, and s in Table 3a become 2300, 21, and 8, resp.), the derived concentrations of K, F, and S become 14.9%, 42.1%, and 41.5%, respectively. For the same altered coefficients but for a water mixture having low color (e.g. Table 3b, 2.5 m depth, Stn. G-2) the absolute change in concentration of the source waters in mixture is much less (in this latter example K, F, and S become 0.7%, 29.9%, and 69.4%, resp.). In this case however, the proportionate change in effluent quantity is greater since the effluent concentration is lower. Note also in the latter example illustrated that for a given change in derived effluent concentration there is a similar change, but of opposite sign, in the derived concentration of fresh water. Conversely, measurement errors in salinity are distributed mainly to the derived concentrations of subsurface zone water and freshwater in mixture. For all cases, however, some proportion of the measurement error in color or salinity is distributed to the derived concentration of all three water sources in mixture, but usually the error contained in one of the derived values tends to be obscured by carrying the computations to one decimal place only.

The derivation of negative effluent concentrations (e.g. Table 4), though not incorrect mathematically, represents an anomaly most likely arising from measurement error in color or from the assumption that the source waters become well mixed in the sampled area. In most cases, errors of expected magnitude applied in all combinations of sign to the source water color coefficients and sample mixtures associated with the negative values could not account for the anomaly. Noticeably, however, the presence of negative effluent concentrations in the data was consistent with the three days of heavy rainfall on August 24-26, inc., as is illustrated by the data for Transect OD in Table 4. During these days, the mean color coefficient for freshwater streams was 2-3 fold higher than usual and resulted mainly from the high color borne by Dakota Creek (Table 2). In addition, stream water run-off was very much higher than usual and the highly colored water from Dakota Creek could be seen jetting well into Thornbrough Channel. Higher freshwater run-off increases estuarine circulation and since the inflow of the largest non-mill color source was seaward of the effluent outfall (Fig. 1), it seems likely that dispersion and mixing of water from this source into the sampling area would be lessened under the conditions of increased rate of seaward displacement of the surface zone water. The anomalous effluent concentrations could be rectified by replacing the color coefficient for freshwater streams on the days of heavy rainfall with values reduced by approximately one-third from those shown in Table 2. Even under conditions of lower stream run-off from the Dakota-McNair Creek system, however, the color coefficient representing freshwater input to the sampled area was probably overestimated because of the seaward location of this largest non-mill color source. Thus the effluent concentrations reported here should be regarded as being on the conservative side, at least by the amount 1.5% concentration, which amount would remove the negative values from the effluent concentration estimates. To better estimate the quantity of this seaward freshwater source mixing into the sampling area and thus improve estimations of effluent concentration, identification of a third property common to four source waters and the use of four simultaneous equations would be required.

The present data do not enable a clear separation of the effects of ebb tide and freshwater inflow on the distribution and dilution of effluent in the study area. However, there was a tendency toward increasing effluent concentrations at most stations after the period of heavy rainfall and when sampling was always on flood tides (e.g. Table 4, August 28-30). On the other hand, some of the highest effluent concentrations were found when sampling on the ebb tide of August 23. A study of the movement of surface drogues released in Thornbrough Channel (Fig. 1) and in the area of the effluent outfall (Landry 1976) indicated that up-channel movement of surface water occurring on a flood tide can persist through the following ebb tide. At other times in that study the seaward movement of surface water on the ebb tide was pronounced, possibly enhanced by the accompanying winds (5-8 km/hr) down channel. The three-day duration of the drogue study limits a generalization of tide-related water movement in Thornbrough Channel. Thus, the indications of transport of effluent away from the outfall (Figs. 3a, c) and greater dilution of effluent (e.g. Table 4) on an ebb tide may reflect local, tide-related events which occur only intermittently in this particular channel.

Winds are an important factor in the movement of inlet surface waters

and can cause the direction of movement to be opposite to the general seaward flow (Bowden 1967). Winds were very light (1-5 km/hr) during the period of sampling but at other times when stronger up-channel winds (15-20 km/hr) were present, the trapping of effluent much closer to shore than usual becomes very apparent. In addition, the marked contrast in color of the surface waters at the edge of the dispersing plume would indicate that a high concentration gradient defines the plume front on the windward side.

The receiving water distribution of kraft mill effluent discharged via submarine diffuser into Stuart Channel, B.C. (Waldichuk 1964), showed some features which are similar to effluent distribution in the much smaller area sampled in the present study. Although a given distribution of effluent in Stuart Channel would probably be related to the particular wind and tide prevailing during the survey, the common pattern was a stratification and dispersion in a relatively thin sheet located mainly at 3-10 m depth (Waldichuk 1964). Dispersion beneath the surface arises from the entrainment of higher density seawater at depth during ascent of the more buoyant effluent which, after rising to the surface above the diffuser, sinks to depths of similar density away from the outfall. In vertical distribution, large cells or masses of effluent were sometimes present beneath the more stratified layers near the surface. Vertical profiles of net current direction and velocity determined in the more comprehensive studies on Stuart Channel indicated that effluent near the surface and at 9-10 m depth would undergo a net transport to the south (i.e. seaward) on the ebb tide but currents at 4-5 m depth would carry effluent in the opposite direction with a greater retention time in the channel expected (Waldichuk 1964). In the present study effluent appeared to be contained largely in the upper 2.5 m of the water column. Surface zone dispersion is probably typical for effluent discharged from surface outfalls, but this dispersing behavior may occur only under conditions of the quiescent sea state that prevailed during the present sampling. When winds are present in Thornbrough Channel effluent could mix to greater depths. However, given the 5-8 m halocline depth (Table I) and the small proportion of surface zone water likely to mix downward through the halocline, it is doubtful much effluent would have an increased retention time in this channel because of up-channel transport in the subsurface zone.

Development of the present method for estimating effluent concentrations in marine receiving waters is based on a highly simplified model of estuarine circulation. Because of the likelihood that circulation in natural systems is more complex than indicated by this model, in its present application the proposed method may be considered robust. An important attribute of the method described lies in the intrinsic correction, in a proportionate manner, for non-mill sources of those properties identifying the effluent. Interfering lignins or lignin-like substances in natural waters, for example, which are particularly troublesome in the Pearl-Benson and fluorometric techniques (Barnes et al. 1963, Wilander et al. 1974), should become less of a problem if a preferred analytical technique is used in conjunction with the method proposed here. The present method does require an additional level of effort to ascertain fundamental oceanographic characteristics of the marine receiving water body and to identify the water sources undergoing mixing. However, the dilution and dispersing behavior of wastewaters in marine systems is an oceanographic phenomenon and it would seem appropriate to incorporate those features in estimations of receiving water concentrations.

ACKNOWLEDGMENTS

I thank Drs. L. Giovando, Institute of Ocean Sciences, and E. Carmack, National Water Research Institute, for helpful discussions in developing this work, P. Futer for technical assistance and Dr. M. Waldichuk for critical comments on the manuscript.

REFERENCES

A.P.H.A. (1971) Standard methods for the examination of water and wastewater. Amer. Pub. Health Assoc. Washington, D.C. 20036.

Barnes, C.A., Collias E.E., Felicetta V.F., Goldschmid O., Hrutfiord B.F., Livingston A., McCarthy J.L., Toombs G.L., Waldichuk M., & Wesley R. (1963) A standardized Pearl-Benson, or nitroso, method recommended for estimation of spent sulfite liquor or sulfite waste liquor concentration in waters. Tappi, 46, 347-351.

Baumgartner D.J., Feldman M.H. & Gibbons G.L. (1971) A procedure for tracing of kraft mill effluent from an ocean outfall by constituent fluorescence. Water Res. 5, 533-544.

Bowden, K.F. (1967) Circulation and diffusion. In: Estuaries (Edited by Lauff G.H.). AAAS Pub. No. 83, pp. 15-36.

Davis, J.C. (1976) Progress in sublethal effect studies with kraft pulpmill effluent and salmonids. J. Fish. Res. Board Can. 33, 2031-2035.

Davis, J.C. & Mason B.J. (1973) Bioassay procedures to avaluate acute toxicity of neutralized bleached kraft pulp mill effluent to Pacific salmon. J. Fish. Res. Board Can. 30. 1565-1573.

Gordon, M.R. & McLeay D.A. (1977) Sealed jar bioassays for pulpmill effluent toxicity: effects of fish species and temperature. J. Fish. Res. Board Can. 34, 1389-1396.

Greer, G.L. (1978) Physical and chemical oceanographic data from Thornbrough Channel in the vicinity of the kraft mill at Port Mellon, B.C. Fish Mar. Ser. Data Rep. No. 109, 47 p.

Josefsson, B., & Nyquist G. (1976) Fluorescence tracing of the flow and dispersion of sulfite wastes in a fjord system. Ambio. 5, 183-187.

Ketchum B.H. (1967) Phytoplankton nutrients in estuaries: In: Estuaries. (Edited by Lauff, G.H.) AAAS Pub. No. 83, pp. 329-335.

Landry L.P. (1976) Radar tracking of drift drogues in Pendrell Sound and Port Mellon June and September 1974. Pacific and Marine Science Rep. 76-8. Canada Dept. Fisheries and Oceans, Institute of Marine Sciences, Patricia Bay, B.C.

McLeay D.J. (1976) A rapid method for measuring the acute toxicity of pulpmill effluents and other toxicants to salmonid fish at ambient room temperature. J. Fish. Res. Board Can. 33, 1303-1311.

Mamayev O.I. (1975) Temperature-salinity analysis of world ocean waters. Elsevier Oceanography Series. Elsevier Scientific Publishing Co.

Mrkva M. (1969) Investigation of organic pollution of surface waters by ultraviolet spectrophotometry. J. Water Poll. Contr. Fed. 41, 1923-1931.

Pickard G.L. (1961) Oceanographic features of inlets in the British Columbia mainland coast. J. Fish. Res. Board Can. 18, 907-999.

Pickard G.L. (1963) Oceanographic characteristics of inlets of Vancouver Island, British Columbia. J. Fish. Res. Board Can. 20, 1109-1144.

Proudman J. (1953) Dynamical Oceanography. Dover Publications Inc. New York. 409 p.

Tully J.P. (1949) Oceanography and prediction of pulp mill pollution in Alberni Inlet. Fish. Res. Board Can. Bull. No. LXXXIII. 169 p.

Waldichuk, M. (1964) Dispersion of kraft-mill effluent from a submarine diffuser in Stuart Channel, British Columbia. J. Fish. Res. Board Can. 21, 1289-1316.

Werner A.E. & Hyslop, W.F. (1967) Distributions of kraft mill effluent in a British Columbia harbour. J. Fish. Res. Board Can. 24, 2137-2153.

Wilander A., Kvarnas H. & Lindell T. (1974) A modified fluorometric method for measurement of lignin sulfonates and its in situ application in natural waters. Water Res. 8, 1937-1045.

Wildish D.J., Poole N.J. & Kristmanson D.D. (1976) The effect of anaerobiosis on measurement of sulfite pulp mill effluent concentration in estuarine water by U.V. spectrophotometry. Bull. Env. Contam. Toxicol. 16, 208-213.

Table 1. Color and salinity at the halocline depth of water at three stations (see Fig. 1) on the west side of Thornbrough Channel in Howe Sound, British Columbia (color in PtCo Units).

	HS-3			HS-4			HS-5		
Date	Depth (m)	Color	Salinity (‰)	Depth (m)	Color	Salinity (‰)	Depth (m)	Color	Salinity (‰)
77-6-6	8	10	26.6	8	6	26.6	8	5	26.6
6-7	6	6	25.6	6	8	26.2	6	9	25.4
6-8	10	6	27.3	10	6	26.8	8	7	24.4
6-9	8	6	25.6	8	5	26.1	6	8	23.8
6-10	6	7	27.2	6	8	26.0	6	6	26.4
6-13	6	10	23.0	10	6	26.4	10	5	26.0
6-14	8	6	25.7	10	6	26.3	8	6	26.2
6-15	6	10	23.2	6	12	22.2	8	9	24.8
6-16	10	6	26.4	10	8	26.1	10	9	26.4
6-17	8	6	26.4	8	9	26.2	8	6	26.4
Mean:	7.6	7.3	25.7	8.2	7.4	25.9	7.8	7.0	25.6
S.E.M.:	0.5	0.6	0.5	0.6	0.6	0.5	0.5	0.5	0.3
78-7-11	6	5	25.5	6	4	26.4	4	5	24.2
8-10	6	3	25.6	6	4	25.9	6	4	26.1
8-18	8	5	26.9	6	7	26.2	4	7	26.6
Mean:	6.7	4.3	26.0	6.0	5.0	26.2	4.7	5.3	25.6
S.E.M.:	0.7	0.7	0.4	0	1.0	0.1	0.7	0.9	0.7

Table 2. Color and salinity coefficients for two water sources (kraft mill effluent and mean for freshwater streams) used in derivations of source water concentrations for each sampling day. The coefficients used for the subsurface zone water source (color = 5; salinity = 26.2‰) were the same for all computations (see text). Units: color (c), PtCo units; Salinity (s), ‰.

Date (08/78)	Sampling time (h)	Water Sources: Effluent		Rainy River		McNair Creek		Dakota Creek		Mean freshwater	
		* c	s	c	s	c	s	c	s	c	s
23	1315-1600	2390	0.9	7	0	5	0	30	0	14	0
24	1710-1900	1530	0.7	25	0	28	0	125	0	55	0
25	1400-1600	1550	0.8	8	0	10	0	75	0	22	0
26	1130-1300	1670	0.7	13	0	33	0	115	0	54	0
28	1345-1515	2400	1.0	5	0	8	0.8	56	0	23	0.3
29	1400-1530	1790	0.9	4	0	8	0	46	0	19	0
30	1345-1515	1800	0.7	2	0	3	0	50	0	18	0

* effluent color interpolated from Fig. 2 at start of sampling time

Table 3. a. Example presented in matrix form of the derived concentration of three source waters (pulpmill effluent, freshwater, subsurface zone water) in mixture, each identified by the properties color and salinity. The source water coefficients are contained in the 3 x 3 matrix, the color and salinity of a water mixture sample in the column matrix.

b. Concentration (percent) of three source waters in the surface zone of marine receiving waters adjacent to a kraft mill. Data from two stations sampled over the depth 0-2.5 m (Transect G: August 30, 1978).

a.

	Source water				Receiving water concn.		
	l_k	f	s	sample mixture	*K	F	S
Color (PtCo units):	1800	18	5	325	17.5%	41.0%	41.5%
Salinity (%):	0.7	0	26.2	11.0			
	1	1	1	1			

[1]Symbols: k, K - kraft mill effluent
f, F - freshwater sources
s, S - subsurface zone water

b.

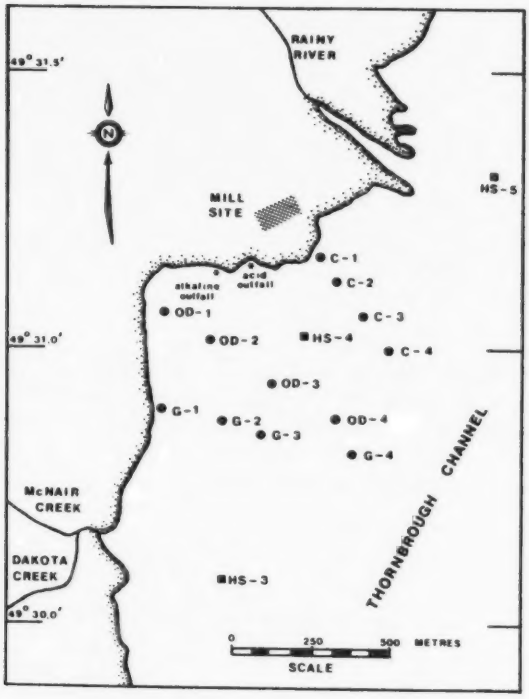
	Stn. G-1					Stn. G-2				
Depth (m)	Color	Salinity	%K	%F	%S	Color	Salinity	%K	%F	%S
0	325	11.0	17.5	41.0	41.5	375	13.1	20.4	30.2	49.5
0.5	75	14.7	3.6	40.4	56.0	150	14.7	7.8	36.3	55.9
1.5	75	15.5	3.6	37.3	59.1	75	15.5	3.6	37.3	59.1
2.5	100	16.6	5.1	31.7	63.2	27	18.2	1.0	29.5	69.4

Table 4. Vertical distribution of three source waters (pulpmill effluent, K; fresh water, F; subsurface zone water, S) in the 0 - 2.5 m portion of the water column in surface zone receiving waters adjacent to a kraft mill. Units of measurement are percent concentration. Values in bold print denote sampling days when frequent, heavy rain showers occurred. Data for Transect OD, Stns. 1 - 4 (Fig. 1).

Depth	Date (08/78)	Tide	Stn. OD - 1			Stn. OD - 2			Stn. OD - 3			Stn. OD - 4		
			%K	%F	%S	%K	%F	%S	%K	%F	%S	%K	%F	%S
0 m	23	ebb	5.9	48.1	46.0	41.6	23.5	34.8	31.1	31.0	37.9	26.9	34.3	38.8
	24	flood	**7.4**	**63.4**	**29.2**	**21.1**	**47.4**	**31.5**	**5.4**	**54.3**	**40.3**	**-0.8**	**55.7**	**45.1**
	25	ebb	**1.2**	**64.2**	**34.7**	**4.2**	**74.9**	**20.9**	**6.7**	**63.8**	**29.6**	**2.7**	**73.4**	**24.0**
	26	flood	**27.9**	**61.8**	**10.3**	**12.5**	**75.6**	**11.9**	**4.3**	**66.8**	**28.9**	**3.7**	**68.5**	**27.8**
	28	flood	30.7	56.2	13.1	26.6	40.9	32.5	6.4	51.3	42.3	0.6	56.5	42.8
	29	flood	41.5	35.9	22.6	34.4	43.1	22.5	1.4	57.8	40.8	0.4	53.8	45.8
	30	flood	30.1	38.7	31.3	32.8	50.2	17.1	4.9	49.8	45.3	0.2	43.3	56.5
0.5 m	23	ebb	2.5	47.2	50.3	0.4	47.7	51.9	1.5	46.7	51.9	0.3	46.6	53.0
	24	flood	**3.2**	**53.8**	**43.0**	**2.8**	**53.4**	**43.8**	**0.6**	**51.3**	**48.1**	**-0.7**	**54.6**	**46.1**
	25	ebb	**0.6**	**57.4**	**42.0**	**1.3**	**58.3**	**40.4**	**5.3**	**48.7**	**46.0**	**0.9**	**57.1**	**48.0**
	26	flood	**5.0**	**65.0**	**30.0**	**8.1**	**55.9**	**36.0**	**1.7**	**65.9**	**32.4**	**0.7**	**67.6**	**31.7**
	28	flood	7.8	51.1	41.1	2.1	49.3	48.6	1.5	52.6	45.9	0.5	55.5	44.0
	29	flood	13.4	45.1	41.5	33.0	42.4	24.8	0.8	53.0	46.2	0.3	50.4	49.2
	30	flood	17.6	31.7	50.7	37.1	37.6	25.3	5.7	39.8	54.4	0.0	43.5	56.5
1.0 m	23	ebb	1.1	47.4	51.5	0.5	46.1	53.4	2.8	42.7	54.5	0.2	45.6	54.2
	24	flood	**8.1**	**42.9**	**49.0**	**0.0**	**49.6**	**50.4**	**-1.0**	**49.4**	**51.6**	**-0.9**	**45.9**	**55.0**
	25	ebb	**0.7**	**44.0**	**55.3**	**0.0**	**55.3**	**44.7**	**-0.5**	**45.1**	**55.4**	**-0.4**	**42.8**	**57.6**
	26	flood	**2.2**	**48.3**	**49.6**	**2.1**	**48.3**	**49.6**	**0.3**	**48.6**	**51.1**	**-0.3**	**53.7**	**47.0**
	28	flood	5.3	44.3	50.4	8.7	38.7	52.7	0.3	48.3	51.3	0.2	49.3	50.6
	29	flood	3.9	42.1	54.1	4.2	40.6	55.2	1.6	46.9	51.5	0.3	46.3	53.4
	30	flood	7.8	32.8	59.3	1.6	39.3	59.1	2.8	39.3	57.9	0.0	41.6	58.4
2.5 m	23	ebb	nd	nd	nd	0.8	44.7	54.6	1.6	43.2	55.3	0.7	43.6	55.7
	24	flood	**4.8**	**43.0**	**52.5**	**-0.2**	**46.0**	**54.2**	**-1.0**	**46.8**	**54.2**	**-1.1**	**44.6**	**56.5**
	25	ebb	**0.0**	**36.6**	**63.4**	**0.0**	**35.8**	**64.2**	**-0.4**	**38.2**	**62.2**	**-0.5**	**39.4**	**61.1**
	26	flood	**0.9**	**39.5**	**59.5**	**-0.5**	**41.7**	**58.8**	**-1.0**	**43.7**	**57.3**	**-0.9**	**44.0**	**56.9**
	28	flood	0.8	36.7	62.5	2.2	37.6	60.2	0.0	40.2	59.8	0.0	45.6	54.4
	29	flood	3.7	32.3	64.0	1.5	39.0	59.5	0.0	35.9	64.1	0.0	34.7	65.3
	30	flood	2.2	36.0	61.8	3.4	31.4	65.2	0.1	30.9	69.1	0.0	34.7	65.3

Fig. 1. Location of sampling transects (C, OD, G) and hydrographic stations (HS) for the area of effluent receiving waters adjacent to a kraft pulp mill on the west side of Thornbrough Channel, Howe Sound, British Columbia.

Fig. 2. Time-course of color of kraft mill effluent discharged to receiving waters in Thornbrough Channel, Aug. 23-30, 1978. The vertical arrows denote the interpolated value of the effluent color coefficient (values recorded in Table 2) at the time each day's sampling commenced.


RAINY RIVER
49° 31.5'
N
MILL SITE
HS-5
C-1
alkaline outfall
acid outfall
C-2
OD-1
C-3
49° 31.0'
OD-2
HS-4
C-4
OD-3
G-1
G-2
OD-4
G-3
G-4
McNAIR CREEK
THORNBROUGH CHANNEL
DAKOTA CREEK
HS-3
49° 30.0'
0
250
500 METRES
SCALE

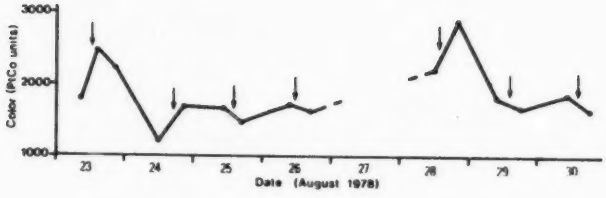
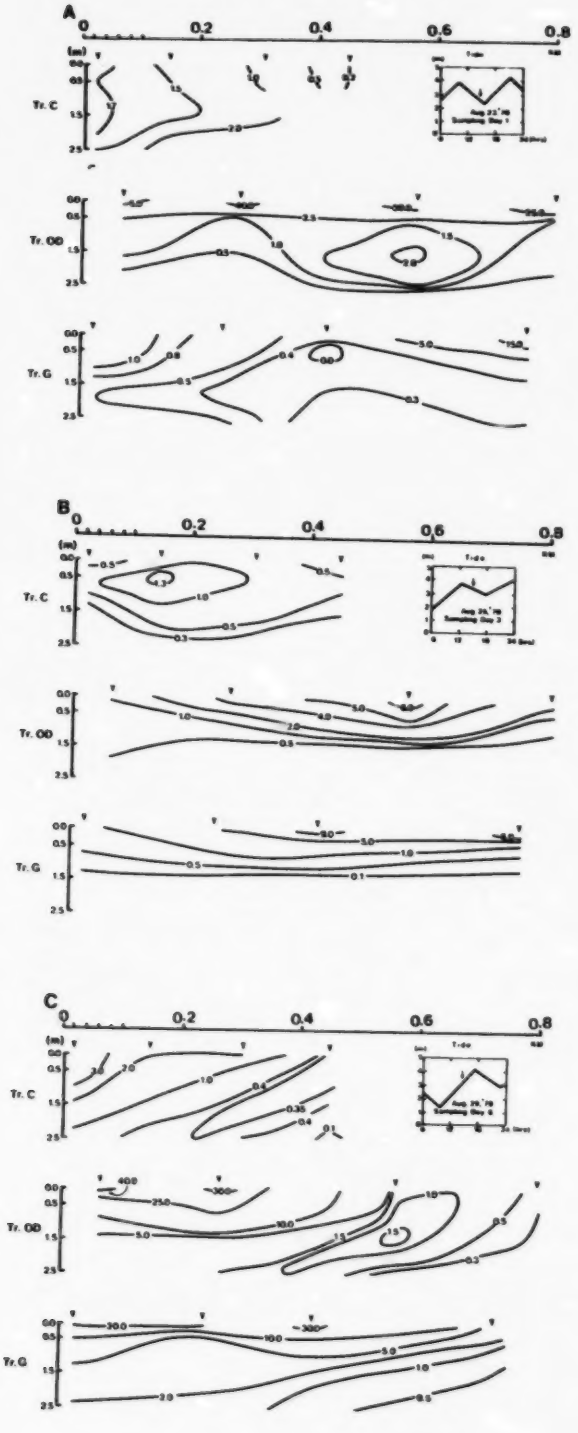

3000
2000
1000
Color (PtCo units)
23
24
25
26
27
28
29
30
Date (August 1978)

Fig. 3. Vertical and horizontal distribution of kraft mill effluent concentration (%) along three transects (Tr.) for three sampling days (panels a-c). Arrow heads denote location on transect and distance from shoreline of sampling stations. Inset: tidal cycle, time sampling commenced (vertical arrows) and sampling date.


A
0
0.2
0.4
0.6
0.8
(m)
Tr. C
Tr. OD
Tr. G
B
0
0.2
0.4
0.6
0.8
(m)
Tr. C
Tr. OD
Tr. G
C
0
0.2
0.4
0.6
0.8
(m)
Tr. C
Tr. OD
Tr. G

POOR

QUALITY

ORIGINAL